

Appl. No. : 09/987,232  
Filed : November 6, 2001

### **AMENDMENTS TO THE SPECIFICATION**

Amendments to the specification below are indicated with insertions underlined (e.g., insertion), and deletions struckthrough or in double brackets (e.g., ~~deletion~~ or [[deletion]]).

**Please amend the title, as indicated below:**

**THERMOELECTRIC ~~HETROSTRUCTURE~~HETEROSTRUCTURE ASSEMBLIES ELEMENT**

**Please amend the paragraph beginning at page 1, line 11, as indicated below:**

The bulk properties of thermoelectric (TE) materials can be altered if the materials are formed from very thin films or segments of alternating materials. The resultant assemblies formed of segments of such thin films are usually called ~~hetrostructures~~heterostructures. Each film segment is the order of tens to hundreds of angstroms thick. Since each segment is very thin, multiple segments are needed to fabricate cooling, heating and power generating devices. The shape, dimensions and other geometrical characteristics of conventional ~~hetrostructures~~heterostructures often make attachment of suitable thermal heat transfer members and electrodes to the individual ~~hetrostructures~~heterostructures assembly difficult. Further complications arise in the extraction of thermal power from the structures. New fabrication techniques, material combinations, and forming methods are required to fabricate TE elements from such materials. New fabrication techniques are even more critical for systems made from thousands of segments since materials formed of many segments tend to be fragile and weakened by (1) internal stresses that result from fabrication, (2) the very nature of the materials and (3) internal weakness caused by contamination and process variation. Further, certain TE materials, such as those based on Bismuth/Tellurium/Selenium mixtures, are inherently mechanically weak and hence, fragile in ~~hetrostructure~~heterostructure form.

**Please amend the paragraph beginning at page 1, line 27, as indicated below:**

~~Het~~structure~~Heterostructure~~ TE materials generally are configured to be long in one dimension (e.g., wires) or two dimensions (e.g., plates). The TE materials are usually anisotropic with varying thermal, electrical, and mechanical properties along different axes. Electric current either flows parallel to a long dimension or perpendicular to the long dimension(s). In TE elements where the current flows parallel to the long dimension, the length can range up to thousands of times the thickness or diameter of the material. To achieve the desired

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performance, such TE elements can be made of a multiplicity of ~~hetrostructure~~heterostructure wires or plates.

**Please amend the paragraph beginning at page 2, line 8, as indicated below:**

Various embodiments using heterostructures in forming thermoelectric elements are disclosed. The ~~hetrostructure~~heterostructures are constructed with layers of bonding and/or intermediate materials that add strength and/or improve manufacturability of completed thermoelectric elements formed of the ~~hetrostructure~~heterostructures. In addition, the bonding and intermediate materials are used in various manners to facilitate or enhance the operation of thermoelectric assemblies. The thickness of the intermediate and bonding materials take into account the desired thermal and electrical characteristics and attributes for the particular configuration or application. Both the thermal conductivity and thermal conductance can be taken into account, in considering the thickness of each bonding and intermediate material.

**Please amend the paragraph beginning at page 2, line 17, as indicated below:**

Several configurations for thermoelectrics are described. One configuration involves a thermoelectric element that has at least two ~~hetrostructure~~heterostructure thermoelectric portions of the same conductivity type (such as N-type or P-type). It should be noted that the use of the term "same conductivity type" in this configuration does not ~~mean~~mean that these portions need to be of the same material, nor doping concentration. An electrically conductive material is coupled to the thermoelectric portions to form at least one electrode.

**Please amend the paragraph beginning at page 2, line 23, as indicated below:**

Preferably, the ~~hetrostructure~~heterostructure thermoelectric portions form layers in the thermoelectric element, and the electrically conductive material is coupled to at least one of the layers at at least one end of the layers. Preferably, the conductive material couples to all or substantially all of the layers, where the electrode is an end electrode. Alternatively, the electrically conductive material may be coupled to at least the top or bottom of the layers.

**Please amend the paragraph beginning at page 2, line 28, as indicated below:**

In one configuration, the ~~hetrostructure~~heterostructure thermoelectric portions form wires or a wire bundle, and the electrically conductive material forms at least one electrode at the end of the wire bundle. Preferably, an electrode is provided for each. Alternatively, the electrically conductive material is coupled to at least the top or bottom of the wires, or separate electrodes are provided for the top and bottom of the wires.

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**Please amend the paragraph beginning at page 3, line 3, as indicated below:**

In one example, a bonding material is between the at least two ~~hetrostructure~~heterostructure thermoelectric portions. The bonding material is advantageously configured to reduce the power density or the shear stress in the element, or both.

**Please amend the paragraph beginning at page 3, line 6, as indicated below:**

An intermediate material may also be provided between the ~~hetrostructure~~heterostructure thermoelectric portions and respective electrodes. Advantageously, the intermediate material is configured to reduce shear stress in the ~~hetrostructure~~heterostructure thermoelectric portions when the thermoelectric element is operated. For example, the intermediate material may be resilient.

**Please amend the paragraph beginning at page 3, line 10, as indicated below:**

In one example, the ~~hetrostructure~~heterostructure thermoelectric portions are of substantially the same thermoelectric material. The ~~hetrostructure~~heterostructure thermoelectric portions may also be constructed of at least two layers of ~~hetrostructure~~heterostructure thermoelectric material.

**Please amend the paragraph beginning at page 4, line 1, as indicated below:**

The at least two layers may also be ~~hetrostructures~~heterostructures, as with the previous example. The ~~hetrostructures~~heterostructures themselves may be made from at least two layers of ~~hetrostructure~~heterostructure thermoelectric material.

**Please amend the paragraph beginning at page 4, line 4, as indicated below:**

Also disclosed is a method of producing a thermoelectric device involving the steps of layering at least two ~~hetrostructure~~heterostructure thermoelectric segments, and connecting at least one electrode to the segments to form at least one thermoelectric element.

**Please amend the paragraph beginning at page 4, line 7, as indicated below:**

The step of layering may comprise bonding the at least two ~~hetrostructure~~heterostructure thermoelectric segments with a bonding material. A further step of providing an intermediate material between at least one of the at least two ~~hetrostructure~~heterostructure thermoelectric segments and at least one electrode may be used.

**Please amend the paragraph beginning at page 4, line 22, as indicated below:**

Figure 1 illustrates a thermoelectric element constructed of thermoelectric ~~hetrostructures~~heterostructures.

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**Please amend the paragraph beginning at page 4, line 25, as indicated below:**

Figure 4 illustrates a thermoelectric element assembly of heterostructures.

**Please amend the paragraph beginning at page 4, line 26, as indicated below:**

Figure 5 illustrates a thermoelectric element portion of a heterostructure.

**Please amend the paragraph beginning at page 5, line 1, as indicated below:**

Several embodiments of thermoelectrics are disclosed where layers of heterostructure thermoelectric materials or thin layers of thermoelectric material form a thermoelectric element. Advantageously, the layers are of the same conductivity type (N-type or P-type) for each thermoelectric element. In one embodiment, the layers are of the same, or at least substantially the same, thermoelectric material. Where the layers are heterostructures, the heterostructures themselves may be formed of layers of thermoelectric material. The layers may be bound together with agents that improve structural strength, allow electrical current to pass in a preferred direction, and minimize adverse effects that might occur to the thermoelectric properties of the assembly by their inclusion. Fabrication of useful TE systems requires a careful understanding of the TE materials' individual properties, such as thermal conductivity, electrical conductivity, coefficient of thermal expansion, properties over the processing and operating temperature ranges, and long-term stability. Often properties associated with other materials used in assembly of TE elements also can affect performance. Often interfacial diffusivity, work function, bond strength and the like are characteristics that arise from the use of combinations of materials and can affect performance.

**Please amend the paragraph beginning at page 5, line 17, as indicated below:**

In systems where the preferred direction of current flow is parallel to a long dimension (e.g., along a bundle of wires or along the long direction of plates), a bonding material for the heterostructures or thermoelectric layers advantageously has low thermal and electrical conductivity, high adhesive strength, and stable general properties that do not change during use.

**Please amend the paragraph beginning at page 5, line 22, as indicated below:**

For systems where the current flows perpendicular to the long dimensions, such as through heterostructures or thermoelectric material layers forming plates, preferred binding agents have high electrical conductivity so that electric current passes through the material with little resistive loss. Preferably, this is achieved by the binding agent wetting the

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TE materials' surfaces either directly, or through the use of an intermediate compatible wetting agent. Advantageous bindings agents also do not degrade the performance of the resultant system either by requiring high fabrication temperatures that could cause diffusion in the TE ~~heterostructure~~heterostructure or promote degradation with time through diffusion, ionic exchange, corrosion or other mechanisms. Figure 1 depicts a TE 100 constructed of TE ~~heterostructure~~heterostructure plates 101 terminated at each end with electrodes 102, 103. The layered plates 101 are assembled with a bonding material 104. The TE 100 may make up one leg or element of a TE module, and is either N or P conductivity type TE material. Generally, many such TE elements are arrayed so that current 105 flows alternately between N and P type materials, with electrodes 102 and 103 making part or all of the current flow path between TE elements 100.

**Please amend the paragraph beginning at page 7, line 6, as indicated below:**

The intermediate conductor material 202 serves to assure uniform, very low electrical and thermal resistance between the TE wires 205 and the electrodes 203. Advantageously, it makes uniform electrical and mechanical connections to every wire. In some configurations, where electrically conductive bonding material 206 is appropriate, the intermediate material 202 makes electrical contact with the bonding material ~~206~~206 as well. The intermediate material 202 can be applied by vapor deposition, sputtering, plating or any other process that forms a suitable electrical and mechanical connection. In addition, the intermediate material 202 can be a solder that wets the wire 205 ends, can be conductive adhesive, can be a flexible or otherwise resilient material that is maintained under compressive force to provide electrical continuity or any other suitable electrical connection mechanism. Further, the intermediate material 202 can itself be made of more than one material. For example, a first layer could be nickel sputtered onto the wires at their ends, and a second layer of tin plating for solderability. A copper electrode 203 could have a copper flash and gold plating for solderability. Finally these two assemblies could be bonded together with solder to form the complete terminator of the assembly 200.

**Please amend the paragraph beginning at page 8, line 23, as indicated below:**

As an example of operation, current 412 passes from the lower electrode 411 through the TE assembly 400 to the upper electrode 401. In this embodiment of the invention, two TE elements both of either N or P conductivity type TE material of the general type of Figure 3 are connected in series by an intermediate material such as solder 406. This can be done for any of

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three principal purposes: (1) reduce the power per unit area produced by the assembly; (2) reduce thermal shear stresses; and (3) make the assembly thicker and more rugged. The first purpose is important since costs of fabricating ~~hetrostructure~~heterostructure TE material increase substantially as the number of layers increases. Furthermore, added layers increase fabrication complexity and reduce yields.

**Please amend the paragraph beginning at page 9, line 3, as indicated below:**

It is important to have the ability to adjust power levels to meet the demands of particular applications. If all else is equal, power density is inversely proportional to TE material thickness. Since ~~hetrostructures~~heterostructures are most easily made thin, power densities can be over 700 watts/square centimeter which is hundreds of times more than that of typical TE modules fabricated from bulk materials. The high heat fluxes that can result can be difficult to transport without substantial losses. As a result, TE performance can be reduced so as to partially or completely negate the higher intrinsic TE performance of the ~~hetrostructures~~heterostructures. By fabricating devices from multiple ~~hetrostructures~~heterostructures, the TE material is thicker and power density can be reduced. TE performance is reduced by the electrical and thermal resistivity of the intermediate materials, electrodes, solder and other materials in electrical series with the TE material, but such ~~loses~~losses are minimized advantageously by careful choice of the materials and how they are mated together. Thermal shear stresses are reduced by making the physical distance between the cold electrode and the hot electrode larger, using multiple layers of the ~~hetrostructures~~heterostructures, and by choosing materials throughout the assembly that have low coefficients of thermal expansion. Also, stresses can be reduced by utilizing intermediate materials that flex easily, such as conductive rubbers, or materials that contain fluids, conductive greases, mercury, other conductive liquids, and any other material that so that they do not transmit significant shear stresses.

**Please amend the paragraph beginning at page 9, line 25, as indicated below:**

In Figure 4, the TE materials 403 and 409 may themselves be layers of ~~hetrostructure~~heterostructure TE materials as in Figures 1, 3, 5, and 6.

**Please amend the paragraph beginning at page 9, line 27, as indicated below:**

Figure 5 depicts a TE element portion 500 formed of ~~hetrostructure~~heterostructure thermoelectric material or thin film layers of thermoelectric material with a first electrode 501, bonding materials 502, 506 and 507, TE plates 503 and 505, and a second electrode 504. The TE

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plates 505 have gaps 509 due to defects or manufacturing tolerances of the TE plates 503 and 505, joints between the plates, or the assembly of many small TE plates into a larger array or the like. Advantageously, the TE plates 503 and 505 are ~~hetrostructures~~heterostructures of TE material and the bonding materials 502, 506, 507 generally cover the surfaces of the TE plates 503 and 505, fill the gaps 509 and electrically connect the plates in the direction of current flow 508. The bonding materials 502, 506 and 507 can be made of multiple materials as discussed in the description of Figures 2 and 3. In this embodiment, the bonding materials 502, 506 and 507 should have moderate to very high electrical and thermal conductivity. If many gaps 509 exist, electrical conductivity of the bonding materials at 506 and 507 and between the stacked plates 503 and 505 should be moderate. In this case, conductivity should not be so high and bonding material thickness so great that significant current flow 508 is shunted through the gaps 509 in the plates 505 rather than through the TE plates.

**Please amend the paragraph beginning at page 10, line 12, as indicated below:**

Figure 6 depicts a TE element portion 600 with electrodes 601, intermediate materials 602, TE plates 603 and 604, and gap 605 in a TE plate 604. In addition, bonding materials 608 are depicted between the TE ~~hetrostructure~~heterostructure layers 603, 604.

**Please amend the paragraph beginning at page 10, line 15, as indicated below:**

As in Figures 3, 4 and 5, current 606 passes through the TE element portion 600 generally upward. In this design, two features are presented. First, the TE plates 603 and 604 are fabricated with an outer layer, not shown, that when processed by heat and pressure or other suitable means, causes the plates 603 and 604 to adhere to one another so as to allow current to pass generally uniformly and with very low electrical resistance through the entire TE element 600. Alternately, and as shown in Figure 6, bonding material 608 can be used to the ~~hetrostructure~~heterostructure layers 603 and 604. [.] The intermediate materials 602 make similar low electrical and thermal resistance connections to the electrodes 601. Second, if the gaps 605 occur sufficiently infrequently in the TE element 600, no special provisions need be incorporated to enhance current flow in them. Similarly, the intermediate material could be omitted if the bond characteristics between the electrodes 601 and plates 603 are suitable for the conditions discussed related to Figure 6. Advantageously the TE layers 603, 604 or ~~hetrostructure~~heterostructure thermoelectric material or thin layers of thermoelectric material.

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**Please amend the paragraph beginning at page 10, line 28, as indicated below:**

Figure 7 depicts a TE element 700 with electrodes 701, ~~hetrostructure~~heterostructure TE plates 702, 703, and bonding materials 704, 706. The current 707 flows generally parallel to a long dimension of the plates 702 and 703. In this configuration, if either a significant number of gaps 705 (or breaks) in the ~~hetrostructure~~heterostructure plates 703 are present or the number of plates 702 and 703 in the stack is small and some gaps 705 or breaks exist, the current 707 will be diverted by the gaps 705, unless the bonding material 704 and 706 (1) fills the gaps 705, (2) possesses the appropriate degree of electrical conductivity, (3) makes good electrical contact between the gaps 705 and the conductive layers that comprise part of the plates 703, and (4) does not contribute significantly to overall electrical and thermal losses in the TE element. Advantageously, distortion of the current flow 708 can be minimized by utilizing a bonding material 704 with electrical and thermal conductivity somewhat lower than that of the TE plates 702 and 703 in the direction of current flow 707. The bonding materials 706 and 704 need to be thin enough or otherwise configured so that they do not contribute significantly to the TE elements' 601 overall electrical or thermal conductivity and thereby reduce TE efficiency.

**Please amend the paragraph beginning at page 12, line 16, as indicated below:**

Although several examples of thermoelectric compositions using the ~~hetrostructure~~heterostructures and binding concepts described herein, the above-described embodiments are merely illustrative and variations from these could be made. For example, thin layers of TE material could be used rather than ~~hetrostructure~~heterostructures in any embodiment. Further, features described in any one figure could be combined with features of any other figure, if appropriate, to achieve an advantageous combination in a particular device. Such combinations are also the objects and teachings of the present invention. Accordingly, the invention is defined by the appended claims, wherein the terms used are given their ordinary and accustomed meaning with no particular or special definition attributed to those terms by the specification.

**Please amend the Abstract, as indicated below:**

Improved thermoelectric assemblies are disclosed, wherein layers of ~~hetrostructure~~heterostructure thermoelectric materials or thin layers of thermoelectric material form thermoelectric elements. The layers are bound together with agents that improve structural strengths, allow electrical current to pass in a preferred direction, and minimize or reduce adverse

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affects, such a shear stresses, that might occur to the thermoelectric properties and materials of the assembly by their inclusion.